Experimental

Materials. Commercial dinitrogen tetroxide was used as previously described (Whitaker and Bennett, 1965). Eastman Kodak Co. white label thianthrene (mp 155-156°) was used without further purification. The chloroform and methylene chloride solvents were reagent grade quality. Merck, acid washed, chromatographic alumina was used for column packing.

Oxidation of Thianthrene to the Monosulfoxide. About 3 g (0.014 mole) thianthrene was dissolved in 200 ml chloroform and a large excess (ca. 20 g) of liquid dinitrogen tetroxide added to the solution. The temperature of the mixture was maintained at 22-25° for about 65 hours. It is important that the temperature not be allowed to rise much above 25° or the yield of the monosulfoxide will be considerably reduced. At the end of this time, the chloroform and nitrogen oxides were removed under vacuum in a rotary evaporator until a yellow solid resulted. Recrystallization from absolute ethanol using decolorizing charcoal gives nearly colorless crystals of the monosulfoxide. Yield after recrystallization was ca. 55 per cent based on the thianthrene used. A slight contamination in the form of the disulfoxide isomers and dinitrogen tetroxide can be completely removed using the chromatographic technique described below. After this purification, mp 141-142° lit. 143° (Shine and Piette, 1962). *Anal.* Calc. for $C_{12}H_8S_2O$: C, 62.06; H, 3.48; S, 27.61. Found: C, 61.85; H, 3.48; S, 27.58.

Oxidation of Thianthrene to the Disulfoxide. About 3 g (0.014 mole) thianthrene was dissolved in 150 ml. chloroform in a three-necked flask fitted with a stirrer, thermometer, and condenser, and a large excess (ca. 40 g) of liquid dinitrogen tetroxide added to the solution. The temperature was held at 35-40° while the mixture was stirred for 40 hrs. The volatile materials were then removed under vacuum in a rotary evaporator until a solid formed. Purification and separation of the *cis* and *trans* isomers was effected chromatographically. The yield of disulfoxide was essentially quantitative. After separation of the isomers, it was found that the *cis* form had constituted approximately 55 per cent of the mixture and the *trans* form about 45 per cent.

Cis, m.p. 289° lit. 292° (Cairns, Eglinton, and Gibson, 1964); *trans,* mp 246-247° lit. 245° (Baw, Bennett, and Dearns, 1934).

Anal. Calc. for $C_{12}H_8S_2O_2$: C, 58.06; H, 3.26; S, 25.82. Found: *cis*: C, 57.80; H, 3.57; S, 26.11. *Trans*: C, 58.15; H, 3.23; S, 25.85.

Chromatographic Purification and Separation. A column 71 cm long and 1 cm in diameter was packed with 50 g of alumina. Methylene chloride was used both as solvent and eluent. About 0.5 g of the oxide to be chromatographed was used each time. A flow rate of 15-20 drops/min. was found to be satisfactory. In the case of the disulfoxide isomers, break-through usually occurred rapidly with the *cis* isomer contaminated with dinitrogen detroxide. However, after 40-50 ml, pure *cis* was obtained. Approximately 100 ml was required to remove all of the *cis* isomer. Next, the *trans* isomer was eluted in highly pure form. Lastly, any monosulfoxide present was eluted. When the monosulfoxide was the principal product, the disulfoxide contaminants were, of course, eluted first, followed by the pure monosulfoxide.

The contamination of the *cis*-thianthrene disulfoxide by dinitrogen tetroxide probably results from the formation of a rather stable molecular addition compound. For this reason, a small fraction of the *cis*-disulfoxide always remained contaminated, even after numerous recyclings on the column or recrystallizations from a variety of solvents.

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ARMATOBALANUS IN THE MIOCENE OF MARYLAND

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Recent armatobalanid barnacles occur predominantly in the Indo-Pacific region. Notable exceptions among the recent fauna are *Balanus circe* Kolosváry (1948, p. 359), from an undetermined locality in the West Indies, and *B. nefrens* Zullo (1963, p. 590), from several localities along the California coast. An undescribed species, mentioned by Zullo (p. 588), found off the southeastern coast of the United States was identified subsequently as a new species of *Conopea* (Zullo, MS.).

Zullo (1963) and Davadie (1963) both assigned the fossil *B. inclusus* Darwin (1854, p. 299) to the subgenus *Armatobalanus*. *Balanus inclusus* was described from the Pliocene (Astian) Coralline Crag of England. This taxon was also reported from several localities in western Germany by Darwin. All the specimens from Germany, referred to by Darwin as *B. inclusus* "*Var. b*", probably represent a distinct, but related, species. Although the present writer concurs with Zullo and Davadie in the assignment of *B. inclusus* to the subgenus *Armatobalanus*, Davadie's allocation of *B. bisulcatus* Darwin (1854, p. 293) and *B. dolosus* Darwin (1854, p. 295) to this taxon remains questionable at this time.

In the present study the author describes an armatobalanid, new to science, from the middle Miocene of the United States. This species is significant because it is the oldest form definitely referable to the subgenus *Armatobalanus*.

The author wishes to express his gratitude to Dr. Victor A. Zullo, Marine Biological Laboratory, Woods Hole, and to Dr. William K. Emerson, American Museum of Natural History, New York, for their comments on the manuscript. Mr. Anthony D'Attilio, Associate at the American Museum, prepared the illustrations of the new species described herein.

Order THORACICA Darwin, 1854

Family **Balanidae** Gray, 1825

Subfamily Balaninae (Gray), 1825

Genus *Balanus* DaCosta, 1778

Subgenus *Armatobalanus* Hoek, 1913

Type Species. Balanus quadrivittatus Darwin, 1854, Recent, East Indies, by subsequent designation of Pilsbry, 1916.

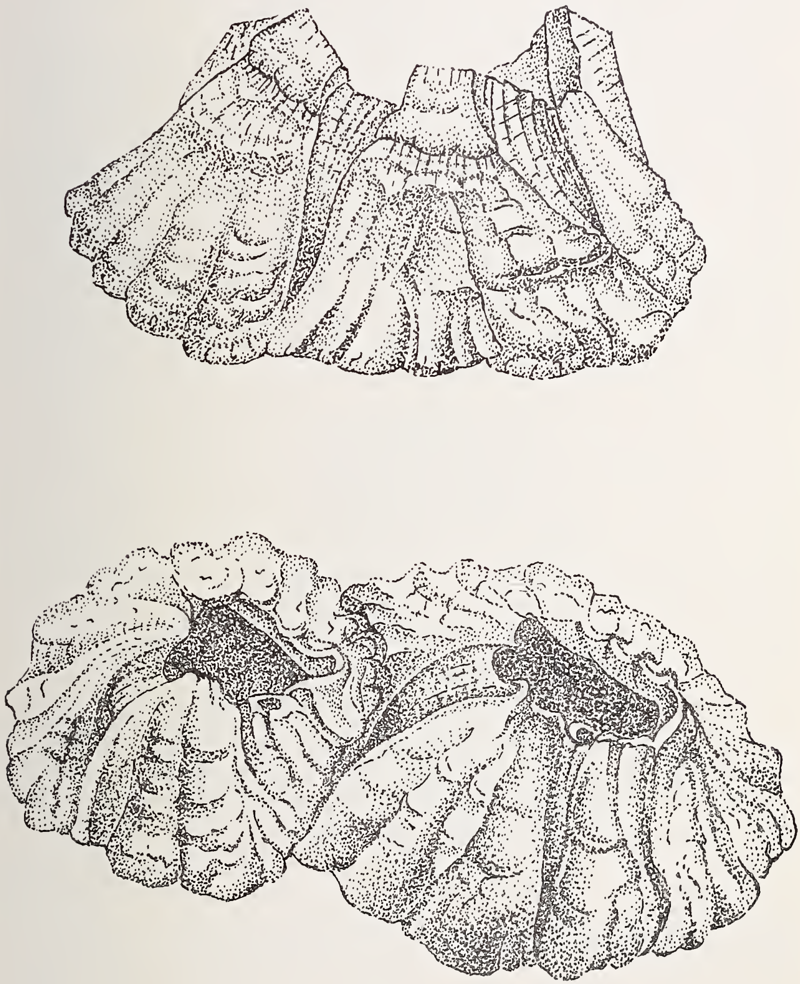

Fig. 1. *Balanus* (*Armatobalanus*) *calvertensis*, new species. Top, lateral view of partially disarticulated shell, carina on right side, holotype, U.S.N.M. No. 649419 (actual height 4.5 mm). Bottom, lateral view of two continguous shells, carina on lower right side, paratype, A.M.N.H. No. 28454/1:1 (actual length of both specimens 10.4 mm).

Balanus (*Armatobalanus*) *calvertensis*, new species

Diagnosis. The shell is small, conic, and well ribbed. Sutural edges of the radii are dentate, and the denticles perfectly smooth. Growth ridges on the scutum are strongly crenate. There is no adductor ridge on the internal surface of the scutum. The basis is flat and possesses radial, non-septate tubes.

Description. The shell is small, low, conic, and somewhat systematically ribbed. The ribs are high, evenly arched, moderately broad, occasionally bifurcating near the base, and they are separated by deep clefts that are narrower than the ribs are broad. When viewed from the apex the periphery of the shell appears scalloped. The peritreme is slightly toothed, and the orifice is pentagonal in shape, it being widest at the rostral end. The carinolateral compartment is narrow, about one-third or less the width of the lateral compartment. Radii are narrow, externally striated horizontally and vertically, moderately sunken below the general shell surface, and they reach to the adjoining compartments. Their summits are inclined, more so than those of the alae. Articulating surfaces of the radii are dentate, but there are no subsidiary denticles either on the upper or lower surfaces of the individual teeth. On the other hand, the articulating surfaces of the alae appear to be devoid of denticles. The sheath occupies the upper one-third to one-fifth of the compartment. Its lower margin depends freely. Behind the sheath there is a very narrow and shallow pocket. Ribs on the inner surface of the compartments are thin, high, and do not reach the sheath.

The basis is flat and tubiferous. The tubes are devoid of transverse septa. The center of the basis is thin, gradually thickening peripherally in the following manner: the basal lamina remains flat while the transverse septa gradually increase in height as they near the perimeter, thus in turn, elevating the superior lamina.

Of the two scuta only the left one was found with the terga and shell. The slightly pectinate occludent margin is one-third again longer than either the basal or tergal margins. The valve is concave between the base and apex. The basitergal angle is truncate, rapidly rising from the basal margin proper to the tergal margin. There is also a slight indentation in the basal margin at the basi-rostral corner. Consequently, when viewed externally the basal margin appears sinuous. Ornamenting the outer surface are longitudinal striae as well as transverse growth ridges, the latter well developed, the former deeply incised. Thus, the interjunctional areas appear accented, presenting a crenate appearance. There are no longitudinal striae on the inflected tergal segment. The articular ridge occupies about three-fourths of the tergal margin, and it is visible externally. The ridge is prominent, high, reflexed, significantly thinner distally than apically, evenly arched, and it terminates abruptly. The articular furrow is broad and moderately deep. The adductor muscle depression is situated above center, and it is ovate, with the long axis baso-apically oriented. The borders of the depression are clearly defined. The tergal border, however, is greatly thickened and paralleled by a seemingly rudimentary adductor ridge. The pit for the lateral depressor muscle is large, deep, and triangular, and it extends well above the basal margin. The rostral depressor muscle pit is also triangular and deep. The inner apical surface of the valve is devoid of ridging or other markings.

Fig. 2. *Balanus* (*Armatobalanus*) *calvertensis,* new species. Internal view of disarticulated left lateral compartment, paratype, U.S.N.M. No. 649423 (actual height 8.1 mm).

Unfortunately, both of the terga are only partially complete, but the morphological features essential for taxonomic separation are present. The valves are broad, flat, and typically exhibit the

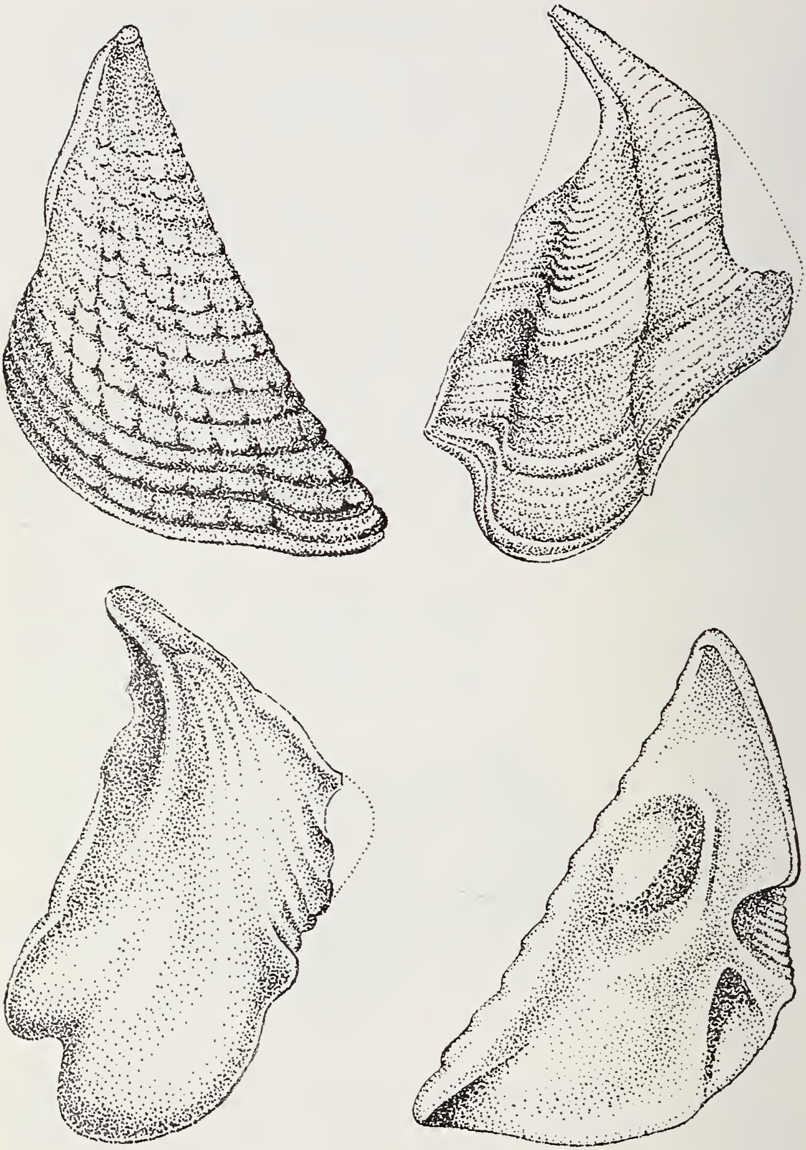

Fig. 3. *Balanus* (*Armatobalanus*) *calvertensis*, new species. Top left, bottom right, external and internal views of left scutum, holotype, U.S.N.M. No. 649420 (actual height 3.5 mm). Top right, bottom left, external and internal views of right and left terga, respectively, holotype, U.S.N.M. Nos. 649421 and 649422 (actual height 3.2 mm).